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TECHNOLOGY HANDBOOK

Technology Utilization Division

SPACE BATTERIES



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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FOREWORD

The development of space vehicles has put new and severe demands on our scientific and engineering talents. One of the most pressing problems faced is that of generation and storage of electrical energy aboard such vehicles. To say that this problem is of extreme importance is indeed an understatement. Subsequent to launching, scarcely a factor is more vital to successful operation of the spacecraft than reliable performance of its power system.

The designer of a battery space-power system must choose batteries, charging methods, and a myriad of circuit components. He must integrate these elements with the other systems of the vehicle, keeping in mind reliability, weight, lifetime, magnetic compatibility, charge-discharge cycle, load, stability at high and low temperatures, heat dissipation, mechanical stability, and still other more subtle factors.

This handbook has been written with the hope of making this task easier. It describes three sealed battery systems—their basic electrochemistry, their characteristics with regard to charging and discharging rates, their behavior on overcharge, their sensitivity to high and low temperatures, their energy storage capability, their life expectancy, and their reliability.

In gathering material for this book, it has become evident that space batteries cannot be considered "off-the-shelf" items like nuts and bolts. The selection of cell types, capacities, types of seals, materials of construction, mounting techniques, and separator materials, for example, must be based on an over-all view of the system as a whole—the day-night ratio, average electrical load, peak load, charge control method, heat removal provisions, number of cycles required, and similar non-electrochemical factors.

The battery field is one in which a great deal of "know-how" has been generated by the several battery manufacturers, much of which is proprietary. The battery companies have been most cooperative, however, in supplying pertinent information for this book.

The development of space batteries is moving very rapidly. Hence, a book such as this cannot long remain up-to-date with regard to performance data. It is hoped, however, that the discussions of the several electro-

chemical systems—their limitations, advantages, and future outlook—will retain more than fleeting usefulness. Furthermore, a mechanism of information exchange is discussed whereby current test data can be rapidly shared among space contractors.

April 1963.

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INTRODUCTION

An energy supply for use aboard a space vehicle could take many forms. The energy source itself might be nuclear, chemical, or solar (ref. 1, 2). Use of solar energy is attractive, because it is available in space and does not require carrying massive supplies of "fuel." Solar energy presents one problem, however, for satellites that spend an appreciable part of their flight period in the earth's shadow. If uninterrupted operation of electrical devices is required, energy must be stored during light periods for use during darkness. Even with nearly continuous illumination, a storage system is necessary if periodic changes in the power demand must be accommodated.

Such an energy storage system might be based on thermal, mechanical, photonic, or electrochemical principles (ref. 3, 4). While all of these have been given consideration for future use, space vehicles have thus far employed electrochemical storage—batteries—almost without exception.

This book is concerned with three secondary battery types: nickel-cadmium, silver-cadmium, and silver-zinc. A word on nomenclature is in order here, since the names commonly used for these three systems are not consistent.

The silver-cadmium and silver-zinc batteries are frequently referred to as "silver oxide-cadmium" and "silver oxide-zinc," respectively, since these terms describe the active electrode components more exactly. The nickel-cadmium battery is practically never referred to as "nickel oxide-cadmium," even though such a term would, perhaps, be more descriptive of the cell chemistry.

In this book, reference is made to nickel-cadmium, silver-cadmium, and silver-zinc batteries, these terms being understood to have the same significance as the longer names.

Only sealed cells are considered, since these are the only promising types for use in space. Furthermore, in discussing the integration of such cells with other power system components, it is assumed that a solar photovoltaic converter is used as the source of charging energy. After a brief discussion of the requirements of space batteries in general, the characteristics of each system are reviewed, pointing out some of the remaining problems.

Since this booklet is intended for use by power-system engineers who are not primarily electrochemists, a brief glossary of terms is included.

GENERAL BATTERY CONCEPTS

BASIC PRINCIPLES

An electrochemical battery—or, more precisely, a “cell”—is a device in which the reaction between two substances can be made to occur in such a way that some of the chemical energy is converted to useful electricity. When the cell can only be used once, it is called a “primary” cell. When the chemical reaction can be *reversed* repeatedly by applying electrical energy to the cell, it is a “secondary” cell and can be used in an accumulator or “storage” battery.

Certain cells are capable of only a few charge-discharge cycles and are, therefore, technically “secondary” cells. Such is the case with certain silver oxide-zinc batteries. These batteries are not capable of the repeated cycling required of a satellite battery system, however, and are, therefore, considered to be “rechargeable primary” rather than storage batteries in this discussion.

To define a battery in another way, it is an arrangement whereby an “electrochemical” reaction can be made to take place so that the “electrical” part of the reaction proceeds via the *metallic* path of the external circuit, while the “chemical” part of the reaction occurs via ionic conduction through the *electrolyte*.

The type of chemical reaction that can be used in an electrochemical cell is known as an “oxidation-reduction” reaction—a reaction in which one chemical species gives electrons to another. By separating the two species and controlling the flow of ions between them, battery engineers make devices in which essentially *all* of these electrons can be made to flow through an external circuit, thereby converting most of the chemical energy to electrical energy during the discharge of the cell.

Before discussing specific battery systems, it is appropriate to point out some components common to all cells. These are:

1. The “cathode” or “positive,” electrode which consists of a mass of “electron-receptive” chemical held in intimate contact with a metallic “plate” through which the electrons arrive from the external circuit.
2. The “anode” or “negative” electrode, which consists of another chemical which readily gives up electrons—an “electron donor”—

similarly held in close contact with a metallic member through which electrons can be conducted to the external circuit.

3. The "electrolyte," usually a liquid solution that permits the transfer of mass necessary to the over-all reaction. This movement takes place by "migration" of "ions"—positively or negatively charged molecular fragments—from anode to cathode and from cathode to anode.

For the three alkaline storage cells considered here, the electrolyte is potassium hydroxide, KOH. The positive ions are potassium, K^+ , and the negative ions are hydroxyl, OH^- . While current flow through the electrolyte involves both positive and negative ions, the cells could operate quite satisfactorily if only the hydroxyl ions were mobile. In fact, cells based on this concept have considerable promise.

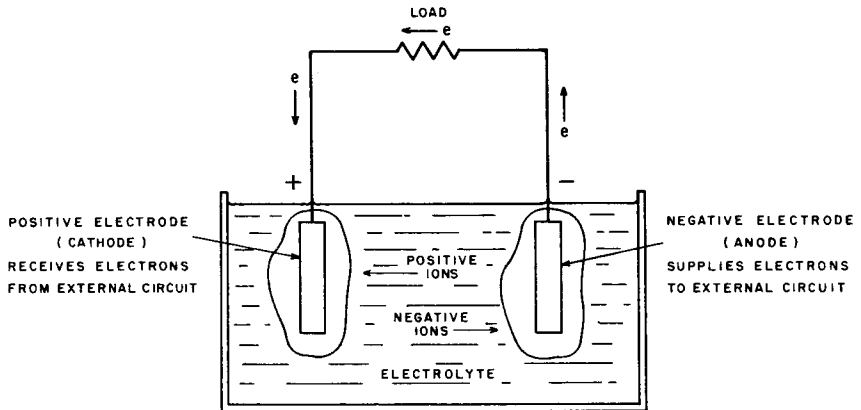


Figure 1.—The elements of a storage cell.

A schematic diagram of these basic cell elements is shown in figure 1. The cell is shown connected to a load—representing the discharge reaction. Charging is accomplished by connecting an electrical source in place of the load, thereby reversing the entire process.

PRACTICAL CONSIDERATIONS

Ideally, the power-system designer would like to incorporate into his circuit design a small, minimum-weight "black box" marked "storage battery," which could be rated at a certain number of volts and a certain number of ampere-hours. Furthermore, he would like to be able to charge and discharge the battery at any convenient rate, at whatever temperature his vehicle happened to provide. He would also like to discharge the battery partially or completely—as demanded by his load conditions—and to "overcharge" it at will if he had surplus charging power during certain

periods. Finally, he would like this battery to last indefinitely, or at least for years.

Needless to say, such a storage battery does not exist. The aim of the developers of space batteries, however, is to come as close to this goal as possible. This section is a general consideration of the limitations in currently available space batteries and of to what problems most research and development attention is being given.

The weight of a battery system can approach, as a minimum, the weight of the active materials themselves. This minimum can be readily predicted, since it is based on the electrochemical constants of the particular chemicals involved. How close this minimum can be approached depends on how skillfully the active materials can be combined with structural components to produce a practical cell.

Thus far, the total weight of sealed cells is five to ten times the weight of the active chemicals. Since storage batteries constitute about 10% of the weight of a satellite, it is apparent that further improvement in the energy-to-weight ratio of such cells is important to the over-all effectiveness of the vehicle.

The charge and discharge characteristics of a cell are also very important to the power system designer. The ideal cell would be chargeable at a voltage only slightly above the discharge voltage, so that the charging system could be as simple and efficient as possible. However, in practical cells, the charge-discharge voltage differential may be quite large—amounting to 0.5–0.7 volt.

The charging efficiency of a cell should be as high as possible, not only for reasons of good power utilization, but so that the production of unwanted heat may be kept to a minimum.

While these cell characteristics are primarily determined by the particular electrochemical system in use, they are also very much a function of the physical operating conditions imposed on the battery system.

The relationship between battery life and severity of service is extremely important and deserves emphasis. When the mission of a vehicle is such that its life must be measured in years, the demands on the battery must be relaxed accordingly. When shorter life can be tolerated, battery service conditions may be more stringent.

The major shortcomings of sealed cells are in the following areas:

1. ability to withstand repeated deep discharge
2. capability for rapid recharge
3. freedom from damage by overcharging
4. wide temperature tolerance.

There is an interplay between (1) and (2) which should be noted. Under the conditions sometimes met in satellite service, the limiting factor in utilization of a battery may be the allowable charging rate. Thus, even if the battery is capable of undergoing deep discharge without damage, it

may be incapable of accepting recharge at the rate required to complete the cycle.

Insensitivity to overcharging is also very important, since greatly simplified charge control circuitry is then possible. Similarly, good temperature tolerance in a cell reduces the need for elaborate heat disposal systems.

All of these factors are interrelated, of course. An improvement from, say, 10% to 20% in allowable depth of discharge for a particular cell system may be equivalent to discovering another system whose electrode reactions have twice the energy-per-pound rating. If a much more elaborate charge control system becomes necessary, however, the weight advantage may be lost.

Obviously, the goal is to achieve the maximum energy per pound from all available systems, consistent with the cycle life required in the particular vehicle and mission under consideration. The charging rate and depth of discharge factors are determined by the battery itself and the details of its construction. Improvements here must be sought *within* the battery. On the other hand, the problems of overcharge and temperature tolerance can be attacked from outside the cell. For example, the use of diodes may be a practical way of controlling overcharge while adding only modestly to system weight.

BATTERY FAILURE

The term "battery failure" in its broadest sense means simply that the battery ceases to accept and deliver energy in accordance with the schedule called for in the function of the vehicle. To the battery engineer, however, battery failure means any one of the mechanical, chemical, and electrical deficiencies which are the basic causes of final failure in electrical performance. Most current research and development effort is, therefore, directed toward improving materials and structural components of secondary alkaline systems, as well as assembly techniques. Detailed approaches to each type of problem will be discussed under the particular cell system involved.

The three most serious cell and battery deficiencies (in the order of importance attached to them by manufacturers, users, and testing groups who were questioned on this point) are separators, seals, and cell uniformity.

SEPARATORS

As discussed earlier, the active materials in a storage battery must remain in the immediate vicinity of their respective electrodes and retain their full electrochemical potency for the life of the battery. To this end, the positive and negative plates are separated by an inert, porous, insulating material. The separators allow ionic migration in the electrolyte, but greatly impede diffusion of the active materials away from the electrodes.

This diffusion of active substances is not a problem with the nickel-cadmium cell, since both are highly insoluble. In the silver-cadmium and

the silver-zinc cells, however, the marked solubility of silver oxide and of zinc oxide demands use of low-permeability separators.

Unfortunately, at the present time there are no separators with the optimum combination of wettability, permeability, inertness toward electrolyte, and resistance to deterioration by reaction with the electrode materials. The reaction problem is particularly serious with silver oxide, an oxidizing agent.

SEALS

To some, a "sealed" cell means one which will not leak electrolyte. To others, it means a "hermetic seal," which will leak neither liquid nor gas at measurable rates, even when high internal cell pressures must be contained. In this discussion, the latter interpretation applies.

There are two classes of "seal": (1) the insulating terminal seal, in which the electrical leads are brought through the cell wall, for which the sealants that have been studied include rubber, plastics, glass, and ceramics; and (2) the case closure, which is usually effected by welding, but also by potting or encapsulation.

The internal pressure which must be contained by the sealing systems varies widely, depending upon the internal construction of the cell and on its operating conditions. It is customary in sealed cells to provide a certain amount of open space within the cell, so that oxygen gas can diffuse readily from the positive electrode to the negative electrode during overcharging. This "starved electrolyte" construction reduces the maximum pressure which the seals must withstand, not only because the oxygen is recombined more rapidly, but because the additional space can hold a particular amount of gas at a lower pressure.

CELL UNIFORMITY

Since satellite power systems always consist of one or more banks of series-connected cells, all cells of one string must be as nearly identical as possible. When differences in electrochemical capacity exist, one or more cells may suffer catastrophic failure as the result of rapid gas generation, with attendant extreme pressures.

This problem is not necessarily avoided by assembling batteries from groups of cells selected for their initial uniformity of capacity. Unless the electrochemical performance of the cells is also quite similar during subsequent charge-discharge cycles, inequalities in charge or discharge efficiencies may develop, leading to different levels of state-of-charge, and eventually culminating in cell reversals or severe overcharge, accompanied by pressure generation and cell rupture.

In general, the problem of cell reversal occurs only when depths of discharge of 50% or greater are involved. At lower depths of discharge, none of the cells of a given series bank is likely to approach full discharge.

Since the total quantity of electricity replaced during charging is always greater than that removed, all cells tend to approach a condition in which they cycle between the fully charged state and a partly discharged state. Only when cell deterioration begins to cause serious loss of capacity in some cells is it likely that battery failure through reversal of these cells will occur.

ALKALINE STORAGE BATTERIES

HISTORICAL BACKGROUND

The first of the alkaline batteries was the nickel-iron system, discovered by Edison in about 1900 and marketed in 1908. It continues to be used in essentially its original form for heavy duty industrial and railway applications. Although they are inferior to the lead-acid battery in power delivery at low temperatures, charge retention, and cost, they have excellent resistance to mechanical and electrochemical abuse.

Closely related to the nickel-iron battery is the nickel-cadmium battery, invented in about 1900 by Junger and Berg. This system retains the mechanical and electrochemical ruggedness of the nickel-iron battery, but has much better performance at low temperature, shows very little self-discharge, and can be hermetically sealed.

Two modes of plate construction have been used: the "pocket" type and the sintered plate type. Only the latter are of significance for use in sealed space batteries, since this construction gives much better high-current and low-temperature performance, due to the larger electrode area and thinner plates.

The superiority of the nickel-cadmium battery over the nickel-iron battery is largely due to the better electrochemical properties of the cadmium electrode as compared to the iron electrode. These advantages of cadmium have been combined with another positive material, silver oxide, which has certain advantages over its counterpart, the nickel positive.

Thus, a cell has been produced which combines the favorable cycling and low-rate discharge characteristics of the cadmium anode with the high capacity features of the silver oxide cathode.

Completing the cycle of electrode substitutions, the high capacity of the silver oxide electrode has also been combined with the high capacity of the zinc electrode, producing the silver-zinc battery. This system has the highest energy storage capability, although it suffers in several other respects in comparison to the silver-cadmium and nickel-cadmium systems.

To establish the chronology of the discovery and development of the several electrode systems, it should be pointed out that the nickel-cadmium cell was developed first (1900), the silver-zinc system next (about 1930), and silver-cadmium last (in the 1950's).

Only in recent years, however, have any of these cells been produced as hermetically sealed units. In this more restricted application, nickel-cadmium is the oldest, followed by silver-cadmium, and joined only very recently by silver-zinc.

Nickel-cadmium batteries have been used in virtually all satellites thus far launched. Good performance has been obtained with silver-cadmium batteries in Explorers XII, XIV, and XV. As of this writing, sealed silver-zinc storage batteries have not been incorporated into any flying vehicles.

Silver-cadmium cells are rapidly approaching a state of development roughly parallel to nickel-cadmium cells, but silver-zinc cells are believed to be a few years behind the others. This view was expressed by Shair (ref. 6) in an earlier estimate of the technical status of the three cell systems.

ELECTRODE AND CELL REACTIONS

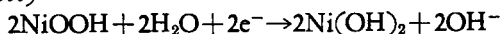
The three battery systems under discussion make use of two different cathodic (positive) reactions combined with two different anodic (negative) reactions. If combined in all possible ways, we would have four cell types:

- nickel positive with cadmium negative
- silver positive with cadmium negative
- silver positive with zinc negative
- nickel positive with zinc negative.

The nickel-zinc cell is the only one of these which has not been developed, largely because it combines the least attractive features of each of the two types of plates, as will be apparent from the discussion which follows.

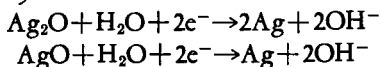
The individual electrode discharge reactions are as follows:

1. *Nickel (positive)*



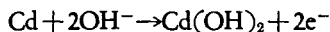
There is some uncertainty as to the degree of hydration of the two nickel hydroxides (ref. 7), but the important fact is that trivalent nickel is reduced to divalent nickel during discharge.

2. *Silver oxide (positive)*



Actually, both of these reactions occur in all silver oxide electrodes, with the first predominating. The second reaction corresponds to the reduction of divalent silver, while the first is the reduction of monovalent silver. The second is the more energetic, as will be seen below.

3. *Cadmium (negative)*



Cadmium shows only a +2 valence, and its oxidation product in alkaline cells is accordingly $\text{Cd}(\text{OH})_2$. An important feature of this electrode is that cadmium hydroxide is essentially insoluble in strong KOH solution. Consequently, it remains in the vicinity of the negative conducting plate and is readily available for charging (compare zinc, below).

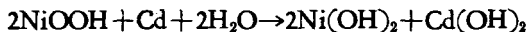
4. Zinc (negative)



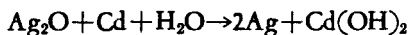
This reaction is written in a form that emphasizes the fact that a considerable portion of the zinc oxidation product is soluble in the electrolyte as zincate ion. This characteristic is the principal drawback of cells based on zinc electrodes.

Putting the various electrodes together in the form of cells yields the over-all reactions for each type of system:

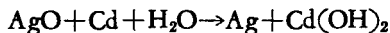
1. Nickel-cadmium



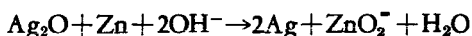
2. Silver-cadmium



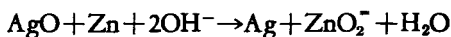
and



3. Silver-zinc



and



Electrical Characteristics

Two distinct sets of electrical parameters must be considered in selecting and developing batteries for spacecraft applications. One is the "theoretical" voltage and specific energy for a given electrochemical system; the other is the "practical" figure which can be achieved in actual hardware. The theoretical values are calculable from the chemistry of the cell and can be thought of as absolute as well as unattainable top values toward which practical cells can be developed.

As pointed out earlier, it is sometimes preferable to select a system with a somewhat poorer theoretical limit, but with better cycle life, greater allowable depth of discharge, good overcharge tolerance, or other features of importance to the particular mission being planned.

The theoretical and current practical figures for the three sealed battery systems are shown in Table I.

Table I. Electrical Characteristics of Sealed Storage Cells¹

Cell type	Ni-Cd	Ag-Cd	Ag-Zn
Nominal open-circuit potential, volts...	1.33.....	1.40.....	1.86.
End of charge potential, volts.....	1.60 at 30° F.	1.60 (ref. 21)....	1.95 (ref. 9).
	1.50 at 80° F.	
	1.45 at 110° F (ref. 26).	
End of discharge potential, volts.....	1.0.....	0.9 (ref. 21)....	1.30 (ref. 9).
Allowable continuous overcharge rate. ²	0.1C (ref. 26)....	0.01-0.02C.....	Very low.
Theoretical specific energy of active ingredients only, watt-hr/lb.	96.....	150.....	215.
Specific energy actually realized in complete sealed cells, watt-hr/lb.	12 (100% discharge depth)	24 (100% discharge depth).	20-50 (in cells capable of a few cycles).
	8 (67% discharge depth).	14.5 (67% discharge depth). 11 (40% discharge depth).	5-8 (in cells capable of several hundred cycles).

¹ Values are at room temperature unless otherwise indicated.

² C is capacity of cell in ampere-hours.

Electrolyte

All three cell systems used the same electrolyte, aqueous potassium hydroxide. The concentration can vary from about 20% to 40% KOH by weight (corresponding to specific gravities of about 1.2 to 1.4). The concentration used varies among the three cell types, and is not critical.

In nickel-cadmium cells, the electrolyte is usually a 1.3 sp. gr. solution of KOH. In silver-cadmium cells, on the other hand, various concentrations have been investigated from 31% to 45% (ref. 8). It was concluded that a level of 40% gave the best performance with respect to minimizing silver migration. In silver-zinc cells a concentration of 40% KOH has been used (ref. 9).

Because the cycle life of alkaline nickel-iron batteries is improved by adding lithium hydroxide to the KOH electrolyte, this additive was also studied for nickel-cadmium cells (ref. 10). The capacity was not improved, but cell voltage was slightly more stable during continuous cycling.

The whole concept of additives to the electrolyte is held in disfavor by battery specialists because such additions usually depress the voltage level of the cells. There are some proprietary additives in use, however.

The relation between KOH concentration and tolerance toward overcharging has been studied for nickel-cadmium cells (ref. 11). A slight improvement was noted when KOH, sp. gr. 1.23, was used instead of sp. gr. 1.31. Even this improvement must be weighed against other requirements; in this case, low temperature performance suffers.

The cell reactions for the three cell types indicate that in each case there should be a difference in specific gravity between the charged and discharged states, thereby making possible a simple "state-of-charge" measurement (as in lead-acid cells). Unfortunately, the change in specific gravity is neither large enough nor reproducible enough to allow charge determination in this way. Because a great deal of hydration of the various active ingredients occurs (largely within the sintered plates) the state of charge cannot be measured reliably.

To summarize, it is clear that major improvements in performance of alkaline cells should be sought in areas other than electrolyte composition.

Overcharge Tolerance

As mentioned earlier, ability of a sealed alkaline cell to accept electrical energy in excess of its nominal electrochemical capacity is a necessary feature of such cells. While elaborate charge-control circuitry can obviate the need for a battery to withstand intermittent or continued overcharging, its ability to do so greatly lessens the complexity of satellite energy-storage systems.

The following example illustrates the importance of overcharge tolerance in determining the required battery weight. A low polar orbit earth satellite is to be powered by a bank of solar cells, using a storage battery to supply the electrical load during periods of eclipse. The charging system is to be constant-current, with no auxiliary charge-control circuitry.

Based on the load requirement, the minimum battery capacity is the product of the load current and the dark time (say, 35 minutes). Based on the minimum available charging time (say, 65 minutes) the charging rate needs to be somewhat more than half the discharge rate (assuming that 30% overcharge is required to fully recharge the battery). Furthermore, during periods of continuous illumination, the battery would need to accept this current as an overcharge current.

If a depth of discharge of 100% is assumed, the discharge rate is approximately $1.7C$ (where C is the capacity in ampere-hours). The corresponding charge (and overcharge) rates are about $1.2C$. This is a rate much greater than can be tolerated by any available cells.

A typical maximum overcharge rate might be $C/6$ (most cells have much lower limits). In the above example, the battery capacity is, therefore, dictated by its overcharge acceptance rather than by load requirements. The battery size needs to be roughly seven times the load requirement, allowing a depth of discharge of only about 15%.

Basically, the ability of a cell to accept an oversharge is determined strictly by its electrochemical properties, as explained below. First, a hydraulic analog is useful. For example, the energy is being stored by pumping water from one reservoir to another at higher level, and the

upper reservoir is closed and has a limited volume, less than that of the lower reservoir. If pumping is continued, the upper reservoir becomes filled and excessive pressure develops. This condition corresponds to a storage cell that cannot accept overcharging.

The upper reservoir is supplied with an overflow line that connects with the lower reservoir. When the capacity of the overflow line is equal to or greater than the amount of water being pumped, no pressure develops. Even if the overflow line has a restricted capacity, the pressure in the upper vessel increases only to the point where the velocity of overflow equals the pumping rate.

The analogy with electrical overcharge is very close. In an electrochemical cell of the type considered here, when *both* of the electrode reactions associated with the charging step have been carried to completion, new reactions take over to accommodate the charging current being forced through the cell. In all cases, these reactions are oxygen generation at the positive terminal and hydrogen generation at the negative one. In time, a few volts of electrochemical potential, driving a cell that is producing hydrogen and oxygen, will generate enough pressure to rupture any container that can be devised.

An obvious way to provide an "overflow" mechanism is to fit the cell with some device that will cause rapid recombination of the gases. Edison patented this idea in 1912 (ref. 12).

A number of problems argue against the recombination approach, however. First, smooth reaction of hydrogen and oxygen requires a catalyst; maintaining the activity of such a device has proved impractical (ref. 13). Second, the ratio of hydrogen to oxygen is rarely 2 to 1, as required for the formation of water.

A much more practical method was discovered many years ago and was applied specifically to nickel-cadmium batteries (ref. 14). In a cell with an oversized cadmium electrode (meaning a cadmium electrode with a higher electrochemical capacity than the corresponding nickel oxide positive) the first reaction to occur on overcharging was oxygen evolution at the nickel oxide electrode (when it became fully charged). This oxygen diffused to the cadmium electrode and (the inventors believed) reacted with the cadmium to produce (uncharged) cadmium hydroxide. Thus, the overcharging current was allowed to produce gas at only one electrode, which then "overflowed" to the other electrode where it was consumed.

The modern view is that the reaction of oxygen at the cadmium electrode is electrochemical, resembling the consumption of oxygen at any electrode where reduction is being effected. That is, it is believed that oxygen is reduced (indirectly) to hydroxyl ion, thus removing the cadmium from any essential part in the cycle.

Nevertheless, when a cell is overcharged at a rate in excess of the rate at which oxygen can be reduced at the cadmium electrode, an oxygen

pressure is developed. If now the charging current is interrupted, the oxygen pressure gradually falls, indicating recombination of oxygen and cadmium.

The pressure developed during overcharging depends upon cell design, temperature, and charging current, of course. As a general rule, cell pressure as high as 100 psi can be tolerated in rectangular cells, while somewhat higher pressure is considered reasonable for cylindrical designs.

With rectangular cells, supporting frames are required, adding weight to the system. Since means are also required for heat removal, however, the advantage of the better natural shape of cylindrical cells is not so great as might be at first presumed.

During overcharge, the oxygen pressure rises in the cell; the rate of oxygen reduction at the negative electrode is correspondingly increased. A steady state is reached in which the rate of reduction equals the rate of oxygen production. The maximum overcharge current which can be tolerated by the cell is that corresponding to the maximum equilibrium pressure of oxygen which can be safely contained in the cell.

At low temperatures, allowable rates are reduced, due to the lower diffusion rate of oxygen through the cell.

An extremely important point is that the rate of oxygen transfer and reduction at the negative electrode must be sufficient to avoid production of hydrogen gas. If hydrogen is produced, cell pressure is raised irreversibly, since no mechanism exists for recombination of hydrogen.

One point should be especially noted. Even under conditions where overcharging can be tolerated with respect to pressure development, the overcharge reactions cause the production of heat which must be taken into account in the over-all thermal control of the battery.

The construction of a cell that can be overcharged without damage, while simultaneously having good cycle life and low internal resistance, requires some compromises in the choice of separator materials.

For good overcharge tolerance, the separator should be thin, highly permeable, and permit rapid diffusion of dissolved oxygen from the positive to the negative plates. High permeability and good wettability also contribute to low internal resistance of the cell, a desirable feature.

A highly permeable, relatively open separator, however, is very undesirable in silver oxide-cadmium cells, since it permits migration of silver oxide away from the cathode.

Since the separator requirements are much less demanding in the nickel-cadmium system, the development of nickel-cadmium cells with good overcharge tolerance has been quite successful. The nickel oxide and cadmium electrodes being relatively insoluble, the use of extremely impermeable separators is not essential.

Other factors, pertinent to the overcharge characteristics of cells, are mentioned in the discussion of separators later in the text.

PLATES

A number of different types of plate structures are used in the three cells under discussion.

By far the most important type of nickel and cadmium plate is the sintered nickel plaque. It is prepared by forming powdered carbonyl nickel around a reinforcing nickel screen or perforated sheet, followed by sintering in a protective atmosphere (cracked ammonia). These plaques are then impregnated with active materials by soaking in solutions of nickel or cadmium salts, followed (in some instances) by electrolyzing in alkali solution to precipitate nickel or cadmium hydroxides. This cycle is repeated several times until the proper quantity of active material has been introduced into the pores of the plate.

Cadmium electrodes have also been made with powdered cadmium metal, cadmium oxide, cadmium hydroxide, or mixtures of powdered cadmium metal and the hydroxide "pasted" on supporting screens or grids of silver or nickel. Such pasted plates are pressed to give rigidity.

Sintered silver plaques may be used in the silver oxide electrode. Another construction is the pasted plate, in which the active material is pressed onto a suitable structure (such as silver wire, foil, or expanded metal) followed by sintering to form a porous, rigid structure.

Zinc electrodes have been constructed by supporting porous zinc metal on silver, cadmium-plated silver, and tin-plated silver grids (ref. 15). Another mode of construction employs a "duplex" structure, in which a porous zinc disk is attached to one face of a silver foil disk. Attached to the other face is a silver-silver oxide disk. These assemblies are stacked alternately with a separator disk to form a series-connected battery (ref. 16).

Details of constructing battery plates constitute a major segment of the body of proprietary information held by battery manufacturers. The ability of an electrode to deliver high currents, to retain capacity upon repeated cycling, and many other electrochemical characteristics depend to a degree on the particular processing variables employed by the manufacturer. These, in turn, have in most cases been developed empirically through exhaustive test programs. Because of the voluminous background of battery art which exists in the patent literature and elsewhere, new developments are frequently believed to be unpatentable and are, therefore, not divulged.

Recalling earlier remarks concerning the basic problem in spacecraft storage batteries—the need for longer cycle life under deep discharge conditions—the design of and method of making cell electrodes is certainly a significant area in which further research must be carried on. The ability of an electrode to maintain "electrochemical contact" with its active material under all conditions of "state of charge" will be the limiting factor in cycle life, once the separator and seal problems have been effectively solved.

An important phenomenon which has been observed in nickel-cadmium batteries is known as the "memory effect." When a battery is continually cycled from full charge to, say, 80% charge (20% depth of discharge), its voltage-time curve during discharge begins to drop abnormally near the 20% discharge level. It is as though the remaining 80% of the capacity has become "inactive," and the battery acts as though it were nearing the discharged state.

It has been found that a sequence of deep discharge cycles restores normal behavior, although use of this technique in a space vehicle obviously complicates the power system.

SEPARATORS

The basic functions of a separator in an alkaline battery are to prevent the positive and negative plates from making metallic contact, to provide a porous structure in which electrolyte can be held, and to prevent unwanted migration and diffusion of the active materials from each of the electrodes.

As mentioned in the discussion of overcharge, the separator has functions which to a degree, at least, are mutually conflicting. Whereas it is desirable to have a low resistance to ionic migration—calling for a relatively open structure with good electrolyte-holding capability—it is also desirable to minimize mass transfer of electrode material particles—calling for a very fine pore structure. This dilemma is complicated further by the requirement that the separator must resist attack by potassium hydroxide and oxidation by silver oxide in the silver oxide-cadmium and silver oxide-zinc cells.

Separators used thus far fall into two principal classes: the relatively open-felted (such as nylon) structures and the film-type products (such as cellophane and ion-exchange films). Extensive studies have been made of the performance of cells made from various separators and combinations of separators (refs. 15, 17).

All attempts to devise a suitable separator for silver oxide cells have been based on the use of multiple layers of different materials, placed in such a way that the best properties of each are used to advantage.

For example, a combination of fibrous sausage casing, woven nylon cloth, and a felted regenerated-cellulose material has been used in silver-cadmium batteries (ref. 18). The ion-migration-restricting and electrolyte-holding properties of the fibrous casing and felted material were combined with the oxidation resistance of nylon, the felted material being placed next to the cadmium.

Other studies (ref. 15) on silver-zinc cells were made with four separator systems: five layers of cellophane, two layers of the fibrous sausage casing, four layers of a polyvinyl alcohol polymer, and a combina-

tion of one layer each of the polymer and cellophane. Again, the intent was to find a separator that resists oxidation yet impedes silver migration and loss of zinc from the anode region. Best results were obtained with the sausage casing, yielding 400-800 cycles.

Because the electrolyte in alkaline cells provides a means for transport of hydroxyl ions from the cathode to the anode during discharge, and vice versa during charge, the ideal separator would appear to be an ion exchange membrane that passes hydroxyl ions only. Stated in electrochemical terms, the transport number of hydroxyl ion in the cell would be unity.

Such a membrane would completely prevent transfer of dissolved substances by diffusion, thereby avoiding loss of dissolved zinc from the anode and silver from the cathode. The membrane material would have to resist oxidation by dissolved silver, of course; but direct contact with solid silver oxide could be prevented by introducing a felted separator of an inert material between the silver cathode and the ion-exchange membrane, as already mentioned.

Certain silver-cadmium and silver-zinc cells are currently being produced with ion-exchange membrane separators (ref. 19). Since the nature of these components is proprietary, however, the above hypothetical remarks may not be applicable, but excellent cycle life is being obtained on these cells (see below).

CASES

Three general types of case construction are used in sealed cells. These are plastic, metal, and a combination of the two in which an inner plastic case is covered by an outer metal case.

The advantages and disadvantages of each mode of construction are summarized in table II.

Another mode of construction is that of "potting," which is discussed later under seals. The chief disadvantage is that of weight.

SEALS

The purpose in sealing the cells of a space battery is two-fold. First, it prevents simple drying out of the electrolyte by evaporation, which would occur rapidly in the vacuum of space. Second, it permits cells to be operated under continuous overcharge conditions, where oxygen is evolved and reaches a certain steady-state pressure.

It is not difficult to prevent evaporation of the electrolyte, since seals for this purpose need resist only modest pressures. To prevent leakage of oxygen during overcharge, however, is extremely important and considerably more difficult (ref. 28).

Table II. Characteristics of Cell Case Types

Type	Advantages	Disadvantages
Plastic.....	No potential on case..... Corrosion resistant.	Strength. Crazing. Heat transfer. Sealing of cover to case. Terminal seal. Shock sensitive. Temperature limitations.
Metal (stainless steel).....	Strength..... Heat transfer. Sealing cover to case (welding). Acts as pressure vessel (in cylindrical cells). Temperature range. Shock resistant.	Potential on case (must insulate case from battery container). Requires insulated terminals.
Combination outer metal case and inner plastic case.	No potential on outer case... Strength. Temperature range. Shock resistant. Provides additional terminal seal.	Difficult inner seal.

In the earlier discussion of overcharging, it was pointed out that the negative electrode is purposely made with a larger capacity than the positive electrode. Thus, overcharging produces oxygen at the positive before the negative electrode is completely charged. The oxygen then diffuses to the negative and is electrochemically reduced. In normal operation, therefore, the negative is never completely charged; accordingly, hydrogen is never evolved. If leakage of oxygen occurs, however, the differential between the capacity of the positive and the negative is reduced. When this differential reaches a certain value, hydrogen begins to be reduced at the negative, and excessive pressures may develop.

Thus, the most important reason for hermetic sealing of space batteries is so that they do not lose their overcharge tolerance through gradual loss of their excess negative capacity.

It is difficult to specify the maximum leakage rate which can be tolerated in a sealed cell. It should be so low that no appreciable change in the positive/negative capacity ratio takes place during the working life of the cell. It is customary to utilize a helium leak detector, which requires that the cell be initially filled with a mixture of oxygen and helium (typical values are 95% oxygen, 5% helium).

This system of inspection is adequate to detect leak rates greater than 10^{-8} cubic centimeter/second, which is the calculated maximum rate tolerable in cells designed for 1-10 years life (ref. 29). Certain disadvantages are evident in this method, however. If the helium is inadvertently omitted from the cell during manufacture, it may appear leak-free while actually not sealed. Similarly, even if the helium is properly inserted in the cell, it may escape by the time final leak testing is carried out, again giving a false indication.

The problem of providing hermetic seals is common to all three alkaline battery systems. Such seals have gone through a number of development stages, the details of which need not be repeated. Early cells utilized plastic or rubber gaskets, which were not sufficiently impermeable to oxygen and which tended to be extruded from their restraining members by the pressure developed within the cell. Although only limited success is now being experienced with pressure-type seals, there is always hope that new materials will be discovered which will permit general use of such seals. Mechanical seals of this type have the advantage of being insensitive to shock and torque loading. Glass seals have been tried but, in addition to their poor mechanical properties, are not particularly resistant to strong caustic.

The latest type of seal involves a ceramic-to-metal bond. It utilizes an aluminum oxide ceramic, nickel alloy terminals, and cell covers whose coefficients of thermal expansions are close to those of the ceramic and the terminals. The actual ceramic-to-metal bond is made with "intermediate bonding metals" and involves "elevated temperatures in a vacuum process" (ref. 20). Although the details are proprietary, this description implies that a brazing process is employed.

Even though such a seal may be mechanically and thermally quite stable, the possibility exists that localized corrosion of a particular zone in the sequence of bonded layers might lead to microcrevices and leakage. This mode of failure is characterized by delayed appearance of a leak, sometimes months after cell manufacture.

In any event, leakage tests continue to be very important hurdles which all cells must clear before they can be accepted for satellite use. This is not to say that a leaky cell might not operate satisfactorily for years in spite of the leak; in the interest of reliability, however, seals must remain intact through the required period of service.

There is no question that leaks are still a major difficulty in sealed cells. Much work in progress is aimed at developing strong, corrosion-resistant, gas-tight seals. Meanwhile, direct inspection for alkali leakage using phenolphthalein, supplemented by the helium test, appears to be the best way to select cells which are sufficiently well sealed.

The helium test is well suited to the detection of leaks in empty cell cases, as an inspection means during cell manufacture.

It is also possible that filled cells might be tested in a reliable manner by subjecting them to an external helium pressure, followed by a conventional leak test. This procedure would circumvent the difficulty introduced if no helium were put into the cell during original filling.

Still another approach to the problem of producing hermetically sealed batteries is the technique of "potting" the cells in a plastic material such as epoxy resin. This has two disadvantages: (1) the potted packages tend to be somewhat heavier and more bulky than the batteries composed of individually sealed cells, and (2) disposing of heat generated within the battery may be troublesome when a heavy plastic layer is used for potting. Otherwise, this approach is quite simple and is cheaper than the other techniques already discussed.

SHELF LIFE

Since satellite batteries are subject to continual charge-discharge cycles, their ability to retain a charge for a long time while on open circuit is of less importance than in other types of vehicles. The relatively slight loss of energy caused by self-discharge is usually small compared with the total quantity of energy handled.

The phenomenon of self-discharge is not completely understood. It is the phenomenon in which one or both electrodes of a cell lose their capacity without current having been drawn through the external circuit. In some instances it is caused by reaction between the active material and the supporting plate; in other cases, the active material may react with the separator material.

Self-discharge on storage of batteries prior to final installation in the vehicle or before launching may be important. As a general rule, batteries should be stored at low temperatures. Fully charged nickel-cadmium batteries stored near 32° F showed negligible loss in capacity in one year (ref. 28).

Losses at elevated temperatures increase sharply. At room temperature, a nickel-cadmium cell will lose less than 10% of its capacity in 3 months. At 140° F, however, it will lose 60% of its capacity in 3 weeks.

Silver-cadmium and silver-zinc cells show even better charge retention than nickel-cadmium, although detailed data are not available.

CYCLE LIFE

The performance of all three types of alkaline cells is continually being improved. The data presented below should, therefore, be recognized to

be merely indicative of the present state of development for each cell system. Only the most recent data are discussed; many of the cycling tests are still in progress (ref. 21-24).

Because of the widely varying conditions under which tests are run, no attempt is made here to present all the details of the several testing programs. Rather, the results are summarized, together with sufficient information on test conditions to make comparisons possible.

It should be pointed out here why there is not a standard method for running all space battery tests. Often the developer of a vehicle must perform only system-oriented tests, not having sufficient time to run a complete parametric analysis on the batteries—even though this might be preferred.

The steps normally taken by a power system designer in the selection of a battery for his vehicle are also pertinent at this point. In general, he uses the battery manufacturer's specifications merely as a guide for an initial choice of cells. Subsequent stages might be as follows:

1. probes various sources for possible cells
2. finds the cell which will be used; invites prototypes (depending on funds)
3. based on response to (2) and on price, decides on source of cells (ideally has a first and second source)
4. establishes "acceptance tests," which must be less stringent than "qualification tests," since the latter might damage the cells
5. after acceptance, makes qualification tests (may not even use acceptance tests).

The life expectancy of cells and batteries, however, can be determined only through cycle life tests. Accordingly, the current state of the art in space batteries is best illustrated in a plot of cycle life as a function of depth of discharge for the three cell systems, as shown in figures 2, 3, and 4.

In the data of figure 2, the criterion of failure for the individual cells was their inability to deliver the required current on the test for a full discharge time (35 minutes). When half the cells of a battery had thus failed, the battery was considered failed also.

In the tests of figure 3, the criterion of cell failure was the end-of-discharge voltage. When cell voltage fell below 0.9 volt before the completion of a discharge cycle, it was considered to have failed.

The data of figure 4 are based on an end-of-discharge voltage of 1.30 volts.

Additional cycle life data have been reported recently for nickel-cadmium cells (ref. 30). The depth of discharge was 36% and the cycle period was 101 minutes. Temperatures studied were 48° F, 90° F, and 110° F. More than 1900 cycles had been completed (September 1962) with no trend toward failure in evidence.

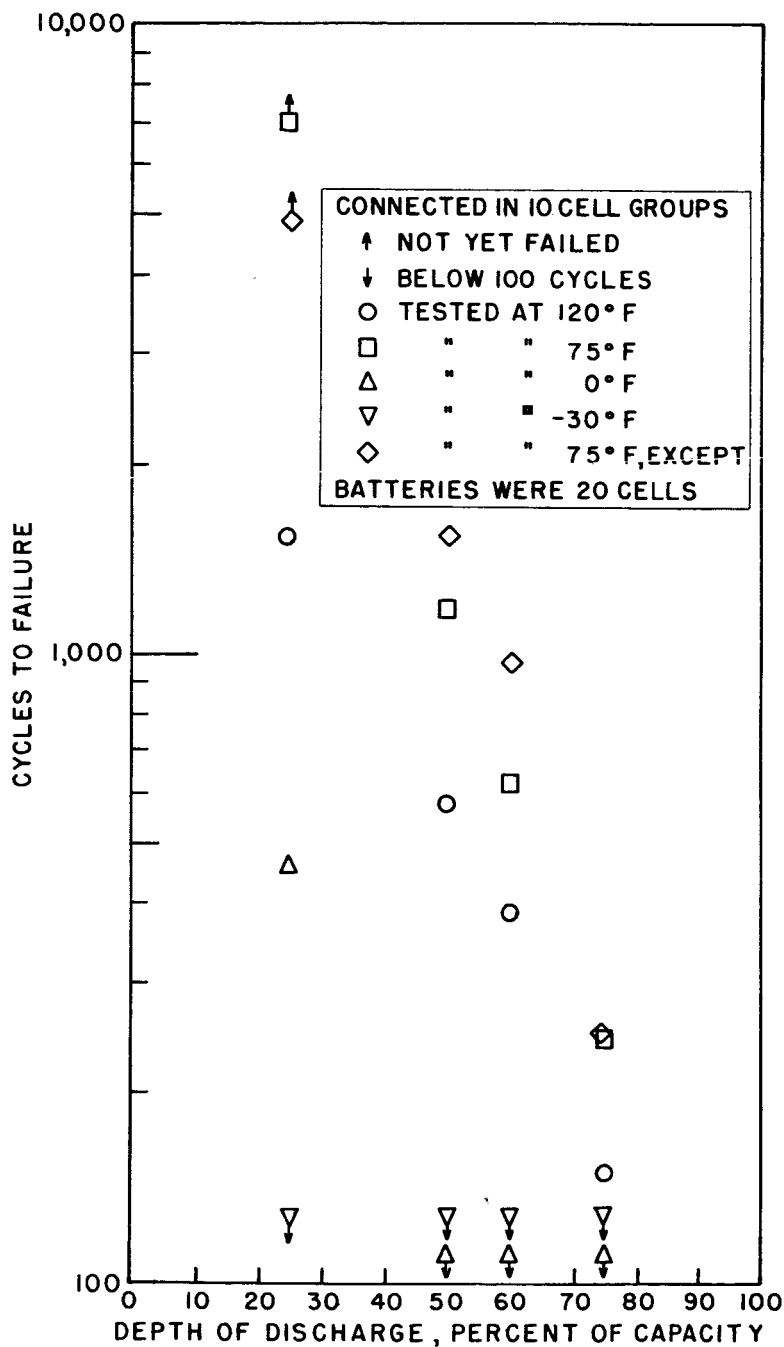


Figure 2.—Cycle life of nickel-cadmium cells. 12-ampere-hour nominal capacity; 90-minute orbit.

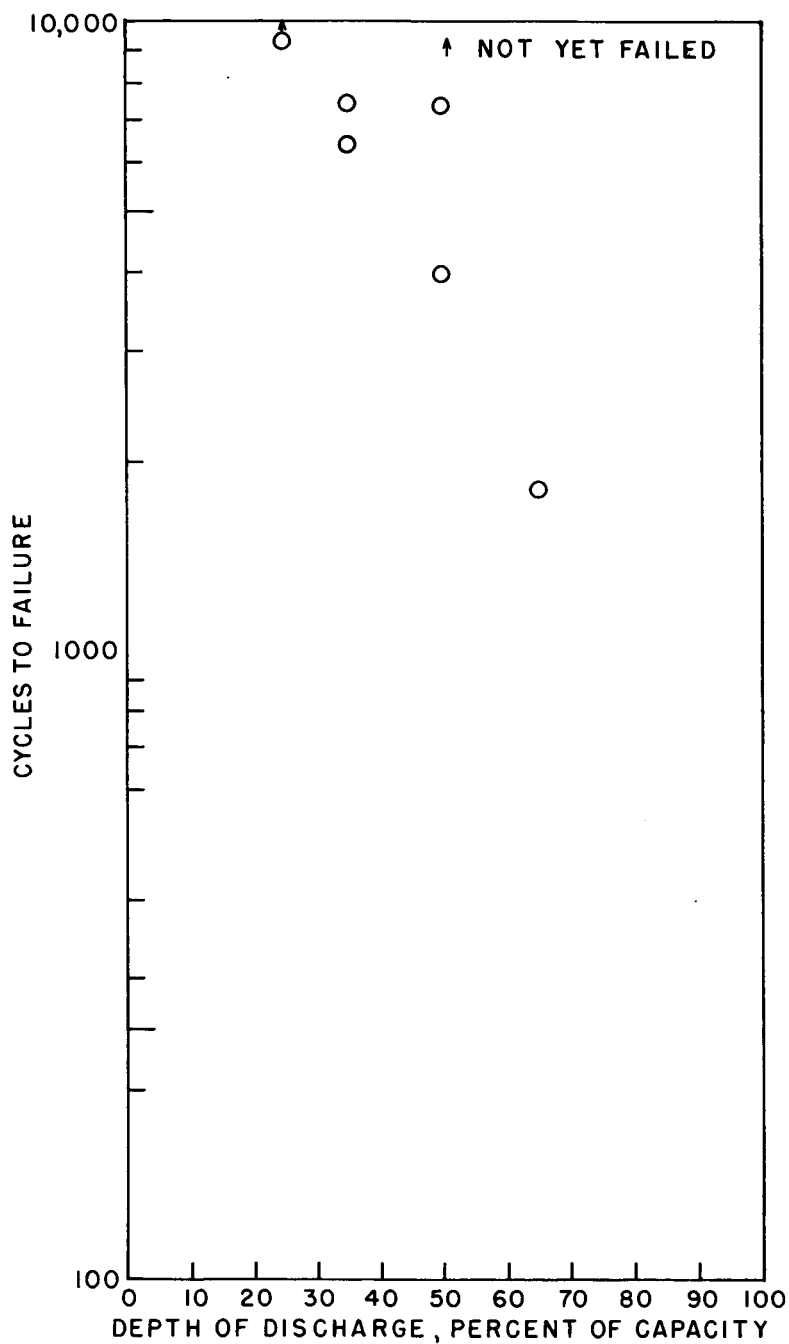


Figure 3.—Cycle life of silver-cadmium cells.

A.—3-ampere-hour nominal capacity cells connected in 3-cell groups; 100-minute orbit at 72° F.

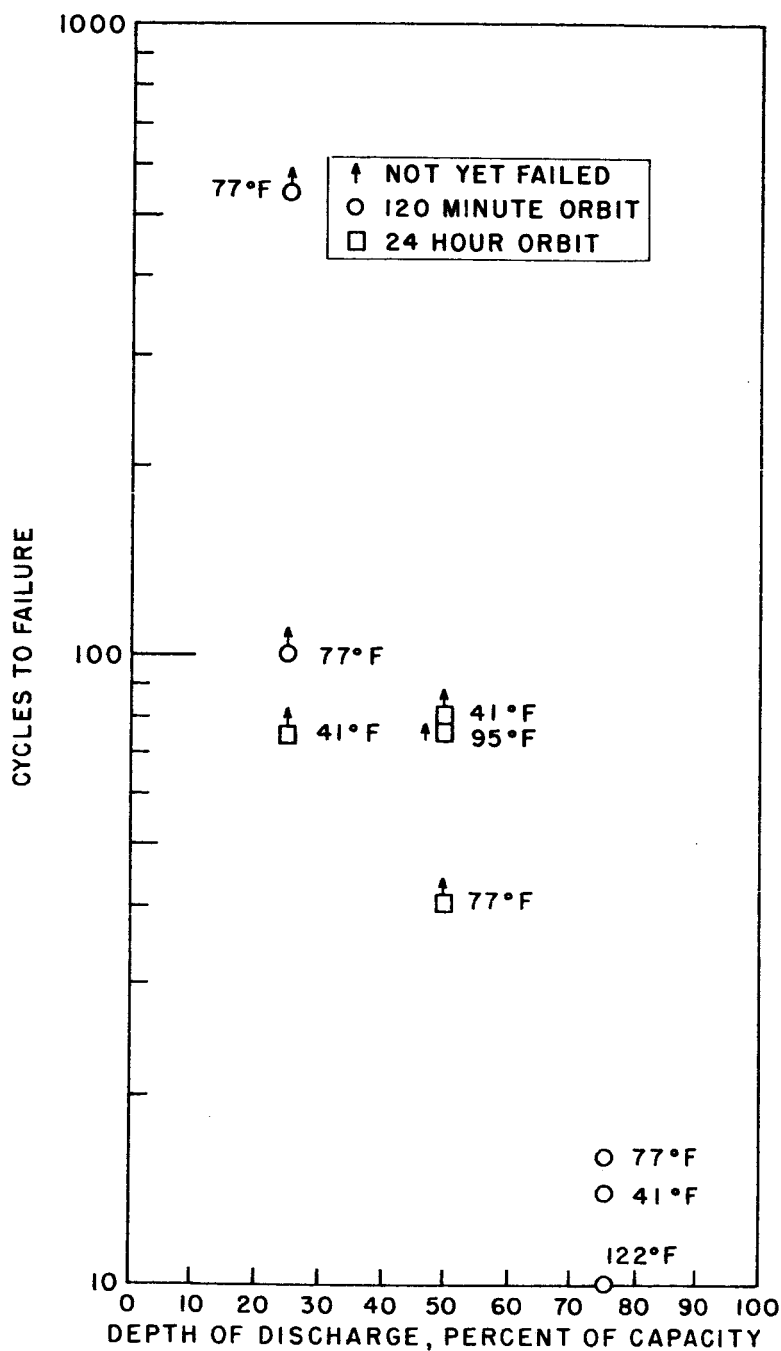


Figure 3.—Cycle life of silver-cadmium cells.
B.—15-ampere-hour nominal capacity cells.

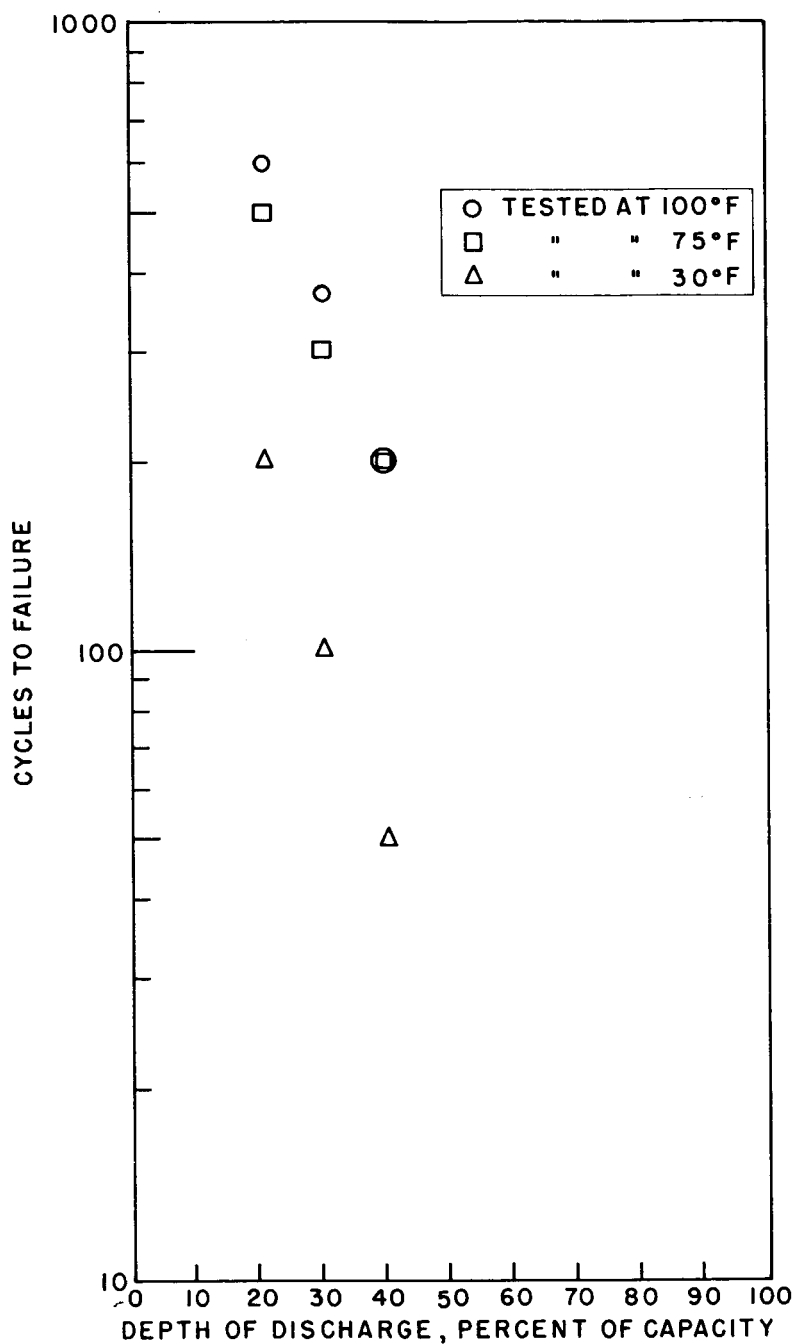


Figure 4.—Cycle life of silver-zinc cells.
A.—25-ampere-hour nominal capacity cells; 120-minute orbit.

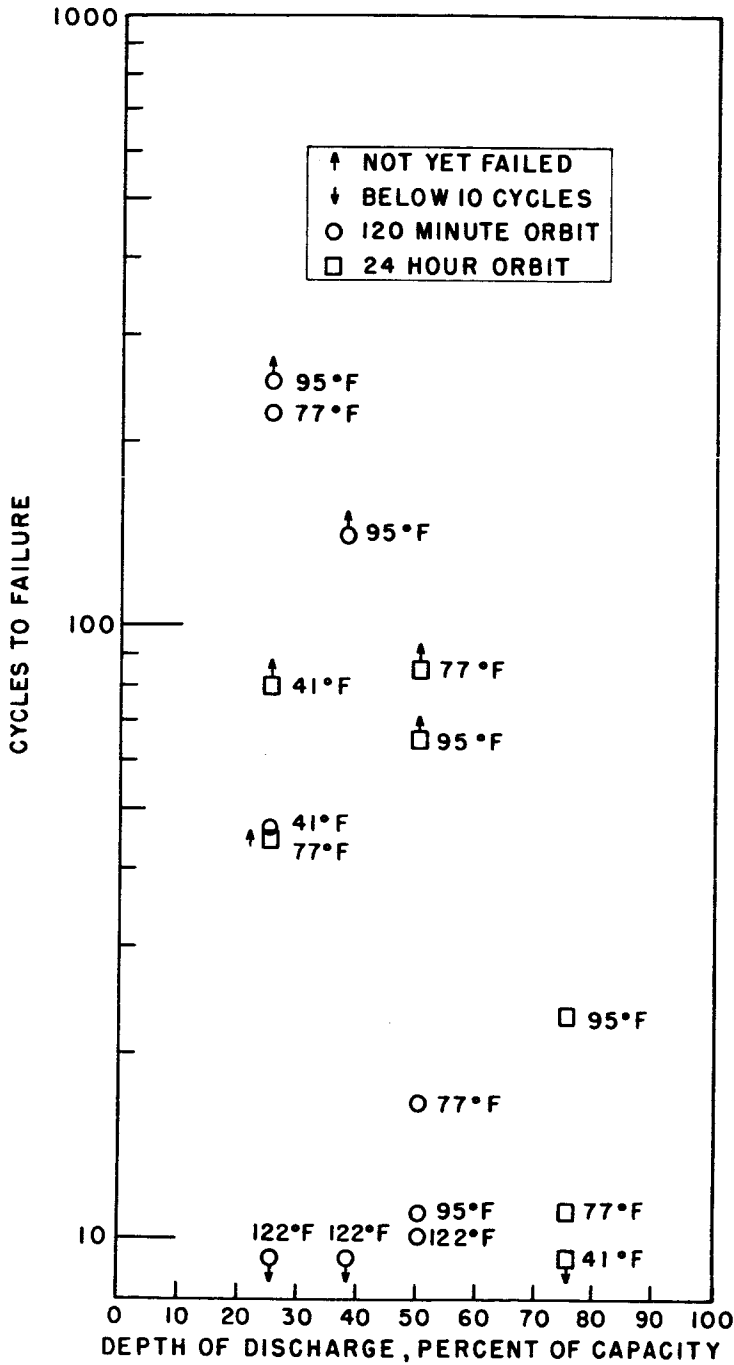


Figure 4.—Cycle life of silver-zinc cells.
B.—25-ampere-hour nominal capacity cells; 120-minute and 24-hour orbits.

Data on 7-ampere-hour silver-cadmium cells of one manufacturer are as follows (ref. 25):

Depth of Discharge, %	Temp., °F	Cycles
17.....	78	2300
34.....	78	2300

These cells were tested in a simulated 90-minute orbit, 55 minutes on charge and 35 minutes on discharge.

CHARGE-DISCHARGE CHARACTERISTICS

The ideal battery for a spacecraft power storage system would have 100% energy efficiency. That is, the battery would deliver the same amount of energy as put into it from the charging source. Such a battery does not exist.

Practical batteries are less than 100% efficient in two respects:

1. There is always a voltage difference between the charging condition and the discharging condition. This leads to an energy inefficiency of 10 to 30%, depending on the cell system and rates of charge and discharge.
2. The basic electrochemical reactions of the battery do not account for 100% of the current passed through the battery. That is, side reactions also occur which consume a portion of the current and cause the battery to have less than 100% coulombic efficiency.

Each of the three cell systems under discussion has its own characteristics with regard to both energy efficiency and current efficiency. Furthermore, each type has certain advantages and disadvantages with respect to allowable charge, overcharge, and discharge rates. These will be discussed for each type, in their approximate order of importance to the power systems engineer.

A. Nickel-Cadmium

A typical charge-discharge curve for the nickel-cadmium system is shown in figure 5 (ref. 26) for a cell, operating at 78° F and at 70% depth of discharge. The data were recorded at cycle No. 500 in a simulated 3-hour orbit. Charging current was 2.4 amperes (120 minutes); discharge current was 4.2 amperes (60 minutes).

The nickel-cadmium cell can be discharged at low and high rates. Using the customary nomenclature, discharge rates from C/8 to 2C may be used. At the highest rate, energy efficiency suffers (60-70%), but the current efficiency remains very nearly 100%.

On the other hand, the charging efficiency (ratio of ampere-hours available to ampere-hours returned) for a nickel-cadmium cell is always less than 100%. Hence, an excess of charge must always be returned to the cell in order to maintain capacity. This necessary total charge may be as

low as 110% of the amount removed (at 30–70° F) and as high as several hundred per cent (at 120° F). The effect of temperature on charging efficiency is so marked that difficulty may be encountered in attempting to restore full charge to a sealed nickel-cadmium cell at 120° F.

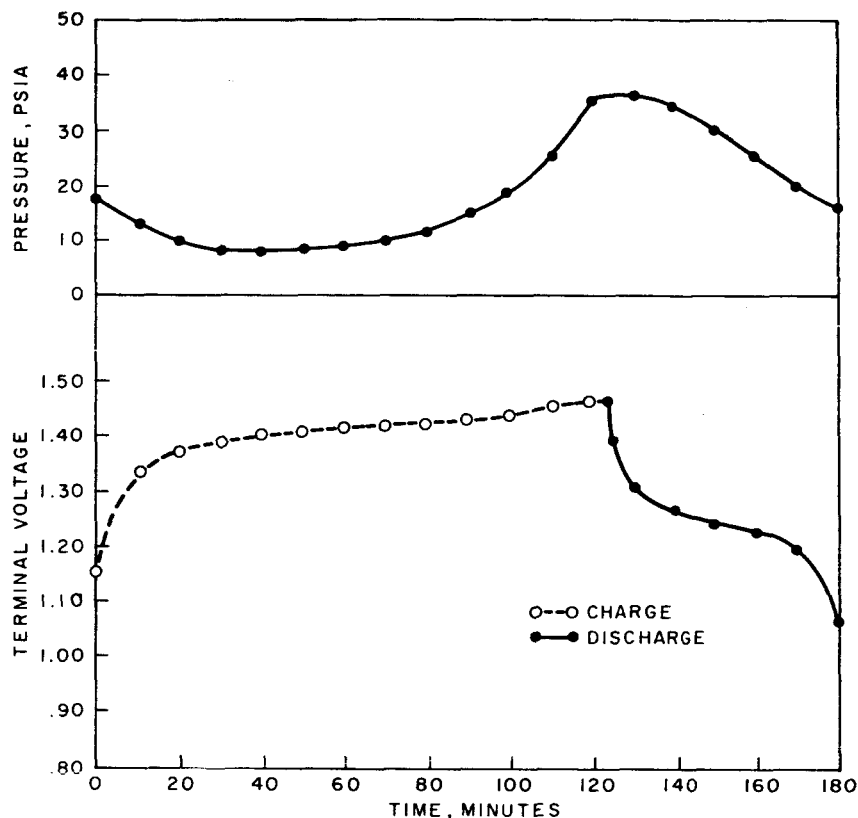


Figure 5.—Charge-discharge curve for nickel-cadmium cell, showing internal pressure changes.

While the discharge rate for nickel-cadmium is flexible, the charging rate is usually fixed by the maximum rate of overcharge to which the cell must be exposed. This again, depends very strongly on the temperature, which controls the rate at which oxygen can diffuse from the positive to the negative electrode during overcharging.

When operated at 70° F, for example, the maximum overcharging (and hence charging) rate would lie between C/30 and C/6, depending upon the particular cell manufacturer. At a temperature of 30° F, on the other hand, the corresponding rate range would be C/200 to C/60. At a temperature of 120° F, much higher overcharge rates would be tolerable (above C/6).

It is obvious, of course, that when a storage battery must function over a range of temperatures, all of the parameters cannot be selected for ideal

battery performance. This is why temperature control is so important to the efficient use of batteries in spacecraft.

Still another restriction must be placed on the charging routine. If the voltage rises above about 1.50 volts, there is danger of evolution of hydrogen gas, which is not reabsorbed (described earlier under overcharge tolerance). It is common practice, therefore, to limit the maximum permissible overcharge voltage to this value. It must be realized that this procedure is only a rough guide for prevention of hydrogen evolution, because the voltage required for hydrogen formation and the voltage required for complete charging both increase with lowering temperature.

A phenomenon which must be avoided in battery operation is "thermal runaway." It occurs when batteries are on "constant voltage charge." As the end of the charging cycle is reached, the overcharge current produces heat. Under certain conditions this heat may lower cell voltage so much that the current increases. The voltage falls further and an "autocatalytic" process has begun, leading to rapid and catastrophic failure of the battery.

Thermal runaway cannot occur if the voltage is reduced after charging is complete or if the temperature is adequately controlled. It does not occur during charging, but during overcharging.

Constant current charging avoids thermal runaway, but may lead to hydrogen evolution (especially at low temperatures, as mentioned above).

The stability of nickel-cadmium cells with respect to deterioration of the electrodes and separator materials is reasonably good. The trivalent nickel hydroxide present in the positive plates is not such a powerful oxidizing agent that organic separators are oxidized. Furthermore, the active materials are quite insoluble, permitting the use of high-permeability separators without loss of plate materials from the vicinity of the electrodes.

At excessively high temperatures, (above about 100° F) the electrolyte reacts with the cellulosic separator materials, causing shorting and loss of capacity.

At low temperatures, the normal cell processes of diffusion and migration are impeded because of increased viscosity of the electrolyte. This is why the permissible overcharge rate is lower at low temperatures. The discharge characteristics suffer also, as illustrated in figure 6.

B. Silver-Cadmium

Figure 7 (ref. 21) is a typical charge-discharge curve for a silver-cadmium 3-ampere-hour cell, cycling at 72° F in a 100-minute orbit, at 25% of discharge. The curve is for one cell of a three-cell battery and was recorded after cycle 1559.

The discharge characteristics of the silver-cadmium system are similar

to those of nickel-cadmium; a wide range of discharge rates may be used without excessive loss of energy efficiency or ampere-hour capacity. At a discharge rate of 1 ampere, for example, a nominal 7 ampere-hour cell showed a capacity of 7.3 ampere-hours. At 7 amperes, a similar cell showed 5.1 ampere-hours.

The major difficulty with silver-cadmium batteries is that they cannot be overcharged at so high a rate as nickel-cadmium batteries can be. Much less permeable separators must be used in silver-cadmium cells in order to control the migration of silver away from the region of the positive electrode. Such separators also restrict diffusion of oxygen from the silver electrode to the cadmium negative, thus causing a higher equilibrium oxygen pressure in the cell for a given overcharge rate. While cells have been made which could be overcharged at C/20, the usual maximum is C/50 to C/300.

The efficiency with which the silver electrode accepts charging current is actually better than that of the nickel electrode, virtually no oxygen being produced until the electrode is about 90% charged.

An attractive feature of the silver-cadmium is its rather sharp rise in voltage near the end of charge. Coupled with the fact that charging efficiency is quite high, this means that charge control based on maximum voltage is a feasible approach for this cell. While it is desirable to have silver-cadmium cells that can be overcharged at rates comparable to nickel cadmium cells, the relative ease of charge control with silver-cadmium makes it attractive for space use.

C. Silver Zinc

Extensive cycling data are not yet available for the silver-zinc system, but figure 8 shows charge and discharge curves for 7.5-ampere-hour cell, under development (ref. 16).

As might be expected, higher rates of discharge cause the voltage-time curves to fall off more abruptly. Similarly, the voltage-time curves become steeper at lower temperatures.

In cells designed for discharge at high rates, cycle life is limited. Conversely, cells constructed with separators selected to restrict diffusion of the active materials away from the electrodes must be discharged at lower rates; otherwise their high internal resistance causes excessive loss of terminal voltage.

In charging, silver-zinc cells suffer the same shortcomings as silver-cadmium cells. They can be charged quite efficiently, but cannot tolerate appreciable overcharge rates.

Typical performance data for cells under development (ref. 9) are as follows:

- room temperature
- 21% depth of discharge

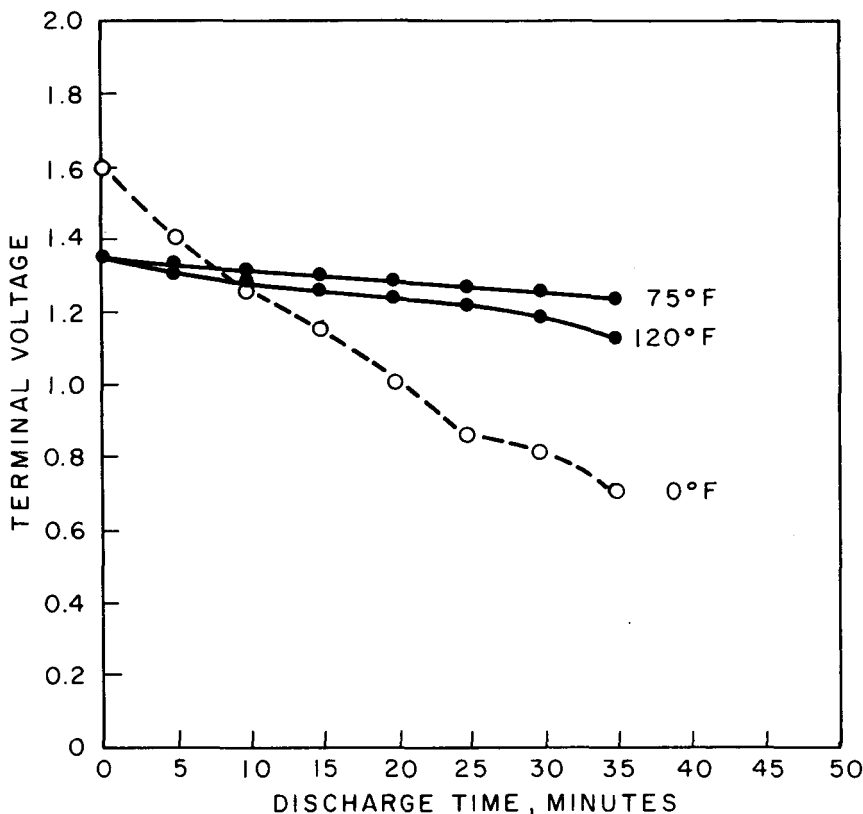


Figure 6.—Voltage-time; curves for nickel-cadmium cells at various temperatures.

discharge at constant resistance load, at approximately $C/2$ to 1.30 volts recharge at constant potential of 1.95 volts, average charging current about $C/7$, tapering from $C/2$ to $C/10$.

Cycle life under these conditions was in the order of 500 cycles, failure resulting from shedding of active material from the negative plates.

ELECTRODE CHARACTERISTICS

It is appropriate to consider each of the four types of electrodes individually, since their behavior largely determines cell properties.

The nickel positive is the only one of the four which requires that an appreciable excess charge be returned to it after discharge. This results from the fact that near the end of charging, evolution of oxygen begins to compete with the oxidation of nickel hydroxide (to NiOOH).

The extent of this effect depends on charging rate and temperature. As a constant temperature, more coulombs must be returned when the charging rate is low than when it is high. For a given charging rate, the efficiency

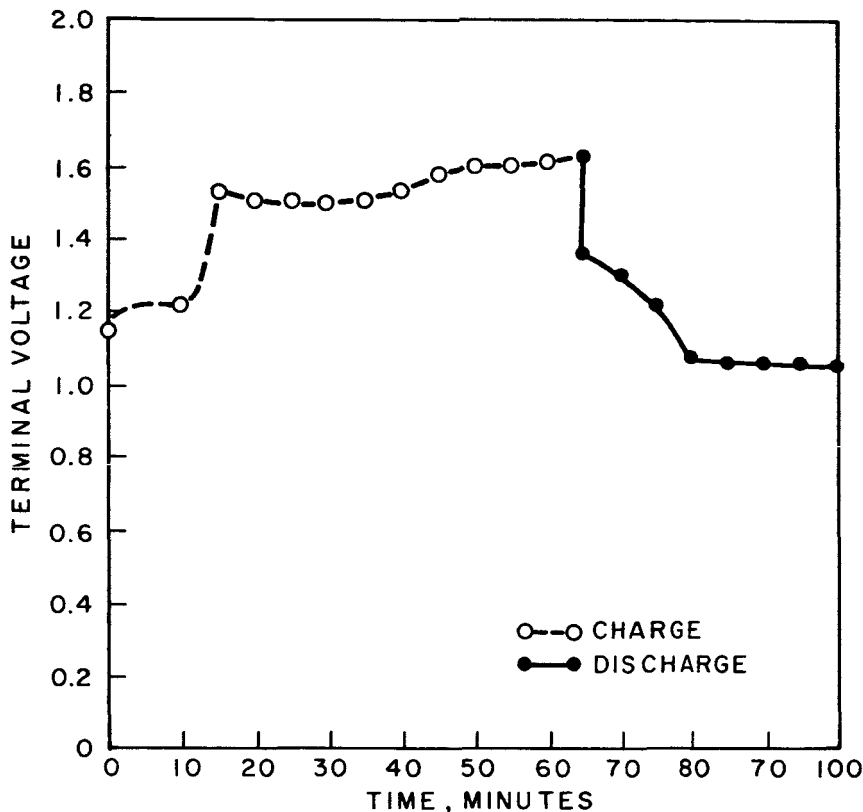


Figure 7.—Charge-discharge curve for silver-cadmium cell.

of charging is much better at low temperatures than at high. As mentioned earlier, it may be impossible to fully recharge nickel electrodes at temperatures as high as 120°F, even at charging rates of C/10 or higher.

The silver, cadmium, and zinc electrodes show much higher current efficiency during charging and generally require only a few per cent over theoretical capacity upon recharging.

The charging curves of the various cell types are determined principally by the curves for the individual positive electrodes, since the negatives are always made with a capacity larger than the positive (see earlier discussion of overcharge tolerance). Hence, the essential concern is with the charging curve for the nickel positive and the silver positive.

The nickel positive undergoes a fairly smooth transition from divalent nickel hydroxide, $\text{Ni}(\text{OH})_2$, to trivalent NiOOH , the electrode potential showing a gradual rise. As the nickel positive approaches full charge, the cell voltage reflects this rise, since the cadmium electrode is still well below full charge.

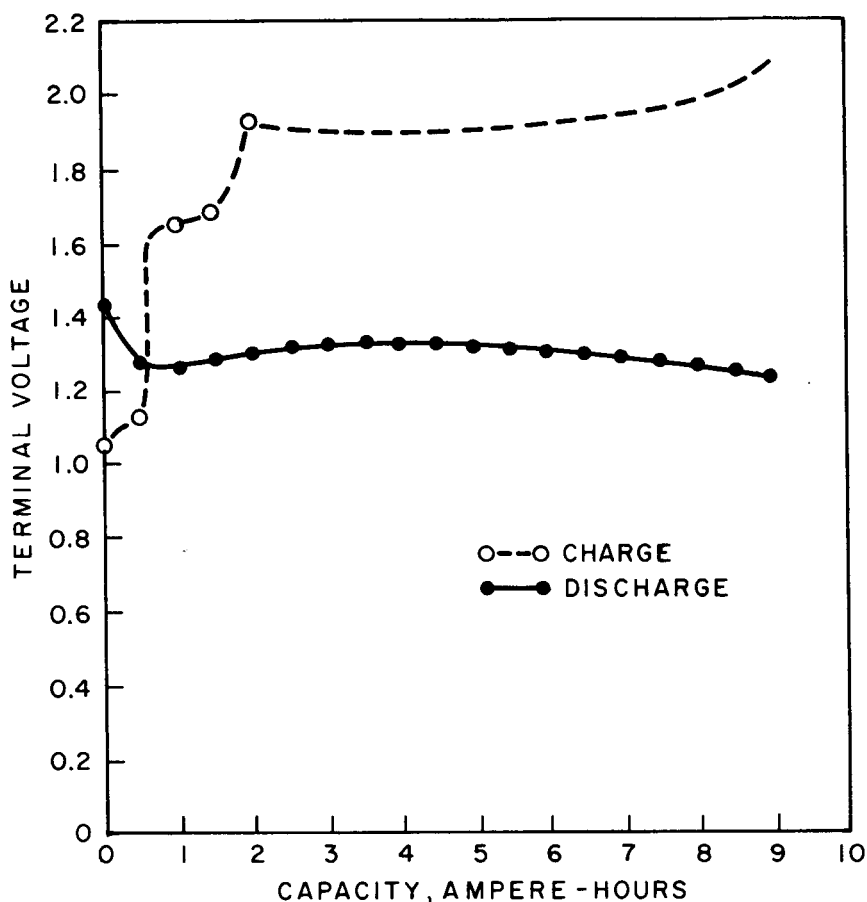


Figure 8.—Charge-discharge curve for silver-zinc cell.

The silver positive, on the other hand, shows two distinct potential levels during charging, corresponding to the monovalent and divalent states of the silver oxide. The point in the charging curve where the transition from the monovalent to the divalent potential occurs depends to a degree on the construction of the positive plate itself, and on the rate of charge.

As the silver positive approaches full charge, the cell voltage rises again, corresponding to the beginning of oxygen evolution. Again, the cell voltage curve reflects primarily the potential changes occurring at the positive electrode, since in both the silver-cadmium and the silver-zinc cells, the negative active material is present in excess.

The marked rise in potential shown by silver cells at the end of charge makes the use of charge control circuits feasible. Zener diodes can be

connected in such a way that, as the cell voltage rises, a larger proportion of the charge current passes through the diode, thus limiting the overcharge rate to a value which will not produce excessive oxygen pressure within the cell.

This approach has the complication, of course, that such diodes will produce heat which must be removed if the control devices are placed within the vehicle. If placed outside, the heat problem can be avoided but the diodes may be damaged by radiation.

The cadmium electrode offers relatively little difficulty in either the nickel-cadmium or the silver oxide-cadmium cell. It forms an insoluble constant valence oxidation product, cadmium hydroxide, $\text{Cd}(\text{OH})_2$, which is completely retained in the plate structure in a condition that permits ready recharging to metallic cadmium. The electrochemical activity of cadmium is such that it does not suffer rapid corrosion during standing; and it is readily reduced during charging without simultaneous evolution of hydrogen.

A serious weakness of the zinc electrode is the tendency for metallic zinc to form loose "trees," which may become physically and electrically detached from the negative plate, causing loss of capacity. If they remain attached, the needle-like zinc deposits may also cause shorting of the cell.

A second difficulty with the zinc electrode is the fact that the discharged form of the active material is soluble in strong KOH solution. Consequently, when zincate diffuses, some of the capacity of the electrode is not available upon subsequent charging. Being a negatively charged ion, the zincate tends to migrate away from the zinc electrode during charging, further depleting the available active material.

Three approaches are being used to combat these two problems: first, the quantity of electrolyte added to the cell is kept to a minimum. This method not only limits the quantity of zincate which can be dissolved, but it improves the oxygen diffusion capability of the cell, and hence its overcharge tolerance (as discussed earlier). It is known as the "starved-electrolyte" method of cell construction.

Second, additives to the zinc electrode material are used in an effort (1) to prevent shedding of the active material, or (2) to cause the zinc metal to deposit during recharging in a smooth, porous, matte form, rather than as needle-like trees.

Polyvinyl alcohol has been studied as a binder material (ref. 9). The additives under study for control of the crystal form of zinc are proprietary.

The third approach to limiting diffusion of ions is use of an ion exchange membrane, as discussed earlier.

BATTERY CONSIDERATIONS IN THE DESIGN OF A POWER SYSTEM

COOPERATIVE DEVELOPMENT NEEDED

While a detailed procedure cannot be presented for the development of an energy storage system for a space vehicle, this section will outline the general course of such a task. A great many personal discussions were held with specialists in all areas of the battery field—manufacturers, users, and testing groups. A number of ideas, opinions, and suggestions were gleaned from these discussions, which are presented here.

By far the most significant opinion expressed during these discussions was that alluded to earlier: batteries for space use cannot be purchased as off-the-shelf items and incorporated into a space power system. The service demand of space systems are so critical that the batteries used in them must be designed or selected specifically for a given system, and must be subjected to extremely close control at all stages in their manufacture.

Because the power system as a whole must be the development goal, close technical contact should be maintained between the battery manufacturer and user. As is the case with many interdisciplinary fields, no one group of specialists is likely to have the necessary background in all of the techniques involved in power-system development. Joint effort by all parties involved, therefore, has been found quite effective.

For example, cooperative development between two manufacturers was quite successful in developing power systems for the Tiros satellites. Similarly, joint development by another manufacturer and the Jet Propulsion Laboratory has been effective in development of the Mariner space vehicle.

Another point which has been stressed heavily by battery users—and is certainly recognized by the manufacturers—is the need for careful control of quality and uniformity in cell and battery manufacture. For example, exceptionally good uniformity of cells that are series-connected is required for maximum utilization of battery weight. Here again, however, the need for an integrated approach to the problem is desirable. For example, the use of semiconductors as "external balancing devices" in a battery system might permit utilization of a great deal more of a battery's capacity in each

discharge cycle than is possible when good series operation depends strictly upon uniformity from cell to cell. Thus, the watt-hours-per-pound figure might be increased by a factor of 10, while suffering an increase of weight due to the control devices might be only 5-10%. This approach may improve the over-all reliability of satellite power systems also (ref. 27).

STAGES IN THE EVOLUTION OF AN ENERGY STORAGE SYSTEM

The design and development of a complete satellite vehicle is a task requiring close integration of many talents. The power system of such vehicles is an extremely important part, as mentioned earlier. Nevertheless, the battery or power system specialist should always keep in mind that flying his section of the vehicle is not the prime objective of the mission. When difficulties develop in other systems of the vehicle, the battery engineer must be prepared to modify his design when this is in the best interest of the main objective.

Periodic design reviews of all systems and components are very valuable in a satellite development program. Such programs are always subject to very close time schedules, and are also subject to many changes. It is well, therefore, for the power systems engineer to be ready to modify the capabilities of his part of the vehicle as demanded.

Shown in figure 9 is a diagram of the several stages through which a battery system development might pass. Reliability is introduced very early in the program; this is quite important. Provision should be made to include, in the manufacturing steps, those tests required to establish the required reliability in the final battery system. When engineering prototype cells are available, a continuing test program should be started, including mechanical, electrical, and life tests. Typical tests which should be included in such a program are shown in table I.

Table III.—Typical Test Program for Prototype Cells

Mechanical-environmental	Electrical parametric test	Life cycling
1. Acceleration under load....	1. Capacity at different rates.	1. Systems-oriented cycling tests.
2. Vibration under load.....	2. Effects of temperature on charge and discharge.	2. Within expected temperature range.
3. Shock.....	3. Safe charging rates.....	3. Continuous overcharge.
	4. End of charge voltages.	

The consensus of specialists with extensive experience in reliability determination and in improvement-of-product through failure analysis was that test programs, per se, may have only limited value unless (1) tests

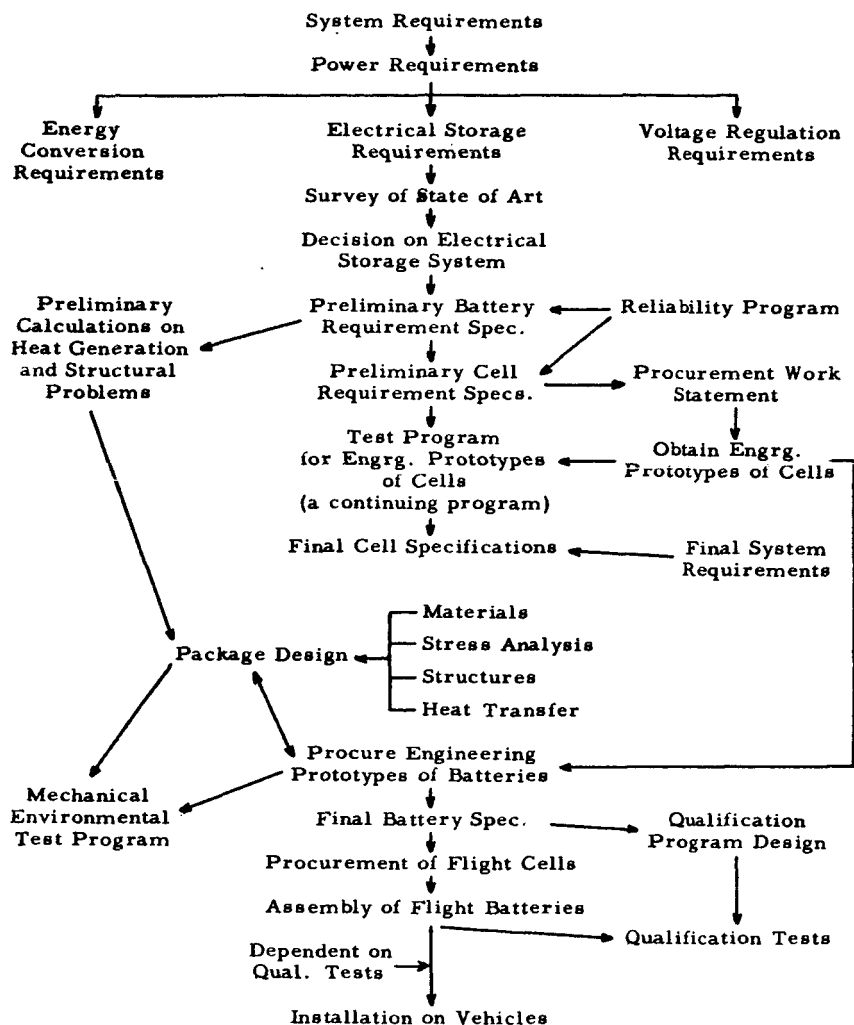


Figure 9.—Organization of a satellite battery development program.

closely simulate actual conditions to be encountered in service, and (2) there is a concomitant quality control program. Furthermore, the view was strong that a failure-analysis program could not be based solely on examination of failed cells; periodic removal of operating cells is imperative.

RELIABILITY

Basic Concepts

While the qualitative meaning of reliability is clear, a formal definition will be helpful. Reliability is the *probability* that a component or assembly

will perform its purpose *adequately* for the period of *time* intended under the *operating conditions* encountered (ref. 31). The italicized words emphasize the four aspects of a reliability assessment. Time is particularly important, being the factor which distinguishes "reliability" from "quality."

As is true of other multicomponent devices, the reliability of space batteries is difficult to assess. This is a discussion of how manufacturers and power system designers have dealt with the problem.

The direct determination of the reliability of a device involves actual operation of a large number of parts under the given conditions, recording the number which survive for the required time. The proportion surviving is the reliability, usually expressed as a decimal.

It is very time consuming and costly to assess battery reliability in this way. A sufficient number of units can seldom be tested for a long enough time to derive meaningful reliability figures. Furthermore, the technology of batteries is constantly changing; improvements are appearing continually, both in materials of construction and methods of fabrication. Consequently, a classical determination of the reliability of a particular cell or battery would very probably have lost its value by the time it was completed.

Reliability can be estimated, however, with a relatively small group of samples, tested over a much shorter time than that required in the final application. Such estimates are based on the theory that the failure rate of a component (number of failures per unit time) is constant over a considerable portion of the failure-rate-vs-time curve. That is, excluding initial rapid failures due to manufacturing defects, and excluding long-time failures due to "wear-out" of the component, the intermediate period will have a constant rate of failure—associated with simple "degradation" of the materials of the device. Using this principle and the mathematics known as the "exponential failure law," the probability of survival can be calculated as a function of time.

The assumption of constant failure rate due to gradual degradation of sealed space batteries may not be valid in many cases. For example, in a cell containing a silver oxide positive electrode and a multiple-layer separator, the reaction between the silver oxide and the organic material will lead to cell failure, but the failure rate will be low during the major portion of the reaction, rising sharply when the bulk of the separator has been penetrated.

Similarly, if zinc trees tend to grow in a silver-zinc cell (eventually causing shorting), there will be no indication of failure until the moment when the short is established.

Thus, there are modes of failure likely in sealed cells which more closely fit the "wear-out" period of the failure curve. When failures of this kind contribute significantly to the reliability figure, the classical failure law, which assumes a "degradation" mechanism, is of doubtful value.

To summarize, direct determination of battery reliability through extensive life testing will give accurate data, but requires a long time and many samples. Extrapolation of short-term tests may yield reliability figures that are not meaningful.

Achieving Reliability

Design

Mature design in the device itself is the most important factor in achieving high reliability. In the relatively "static" devices encountered in the fields of architecture and civil engineering, the confidence with which an engineer can produce a high reliability design is good. In the design of "dynamic" devices such as batteries, however, where the requirements are continually changing, and where data on reliability of component parts are lacking, the path to a mature design is much less clear.

The gradual achievement of better designs for space batteries is being accomplished through continuing test programs on cells and batteries in all stages of development. As mentioned earlier, life cycling tests, accompanied by careful analysis of both failed cells and those removed before failure, can contribute directly to choice of materials and methods of assembly, as well as to discovery of the optimum operation parameters such as charging methods, rate of overcharge, and depth of discharge.

Quality

Assuming that the design of a cell or battery is such that satisfactory performance is possible, the quality of the product is extremely important. Manufacturers of sealed space batteries have set up special production facilities and elaborate testing programs to insure the highest possible uniformity and reliability. There is constant feed-back from the results of these tests, leading to improvements in the basic designs.

Of course, the test programs must be designed to measure the performance of batteries under conditions expected in the mission, as already discussed.

Other Approaches

Many techniques for achieving high reliability are not applicable to space vehicle devices. For example, a valuable principle in land-based equipment is "maintainability." That is, good continuity of operation is achieved by providing for easy replacement of a failed part.

Other approaches commonly used are "redundancy" and "switchover." For space applications these methods have the obvious disadvantage of increasing weight. It is considered preferable to put all available engineering and scientific effort into the improvement of design and quality, with the least possible dependence on redundancy.

ACCEPTANCE AND QUALIFICATION TESTS

When cells are submitted by a manufacturer to the user, it is customary to perform a series of tests sufficiently stringent to insure that the cells meet performance specifications, yet not so severe that the cells might be rendered unfit for use in the vehicle. These tests are known as "acceptance" tests.

Subsequently (or simultaneously) a much more rigorous series of tests is performed on a representative sampling of the production cells of final design. These tests are known as "qualification" or "type approval" tests, and are considered to be so severe as to render the cells unusable for flight.

Extracts from typical acceptance and qualification tests are presented below to illustrate their general nature. In this particular case, the cells were 0.81-ampere-hour nickel-cadmium cells.

A. Acceptance Tests

1. Examination of Product

Each cell is inspected to determine compliance with respect to material, workmanship, dimensions, weight, and product marking.

2. Leakage Test

A leakage test is performed on each cell by one of two methods:

a. Helium leak test (for cells containing helium gas). The cell is placed in a vacuum of 10^{-4} mm Hg and held for 5 minutes with a mass-spectrometer type leak detector, and should not exceed 1 cubic centimeter of helium per month.

b. Electrolyte leak test. If helium leak detector equipment is not available, the cell is swabbed with a 1% alcohol solution of phenolphthalein. If the solution changes color (to red), a leak (of alkaline electrolyte) is indicated.

3. Capacity Discharge Test

The cell is charged at 0.065 ampere for 16 hours at 75° F, let stand on open circuit for 1 hour, and discharged at constant current to the prescribed end voltage of 1.0 volt (nickel-cadmium cells). This test is repeated for a second charge-discharge cycle. The discharge capacity of the cell for each cycle shall meet the minimum originally specified.

4. Charge Retention—Minimum Charge

Following the above capacity test, the cell is short-circuited for 14 hours. The short is removed and the cell charged for 10 minutes (at the charging rate which would normally be applied for 16 hours). The cell is held on

open circuit for 24 hours, during which its voltage shall be 1.16 volts minimum. (This procedure is for the purpose of detecting internal shorts.)

5. Overcharge

Following A-4, the cell is charged at 0.065 ampere continuously for 96 hours, during which time the on-charge voltage shall not exceed 1.48 volts. Following this overcharge, the leakage test shall be repeated (A-2).

6. Shock

The cell shall be fully charged, mounted in a test fixture simulating the final spacecraft installation, and subjected to two 60-g, 5-millisecond terminal peak sawtooth shocks in the direction of the longitudinal axis of the cell. The cell shall be discharged at a constant current of 0.12 ampere prior to, during, and after each shock. The voltage must not fall below 1.2 during 70% of the discharge period, and must not deviate by more than 0.05 volt during the shock pulse.

B. Qualification Tests

A minimum of 20 specimens shall be subjected to qualification testing.

1. Acceptance Tests

All cells are tested in accordance with the acceptance tests just described.

2. Transportation, Altitude, and Temperature Test

The cells (in their shipping container) are held 4 hours in a chamber at -20°F and a pressure corresponding to 50,000 feet. Following this, they are subjected to one charge-discharge cycle test at 75°F .

3. Acceleration

The cells, mounted in a test fixture simulating the spacecraft installation, shall be subjected to the sustained acceleration listed below. The cells (charged beforehand) shall be discharged at a constant current of 0.12 ampere prior to, during, and after each test.

- a. Longitudinal axis of cell—35 g for 3 minutes
- b. Transverse axis of cell—35 g for 3 minutes

4. Spin

The cells, mounted in a test fixture simulating the spacecraft shall be rotated at 206 rpm for a duration of 48 hours. Cells will be 13 ± 1 inches from center of rotation. For the duration of the test the cells shall be continuously subjected to the charge-discharge cycle test of A-3.

5. Vibration

The cells shall be attached firmly and securely to a vibration exciter without attempt to simulate the spacecraft installation. The assembly, case or container, should be loaded in such a manner as to make it dynamically similar to the flight configuration. The vibration level shall be observed on the exciter as near to the supporting bracket as possible. The cells shall be subjected to the vibration test in a direction parallel to the cell axis and in a direction perpendicular to the cell axis as listed below. (The thrust axis is defined as the parallel axis.)

Axis	Frequency range, cps	Duration, minutes	Acceleration, g (rms)
<i>a. Sinusoidal</i>			
Thrust.....	5-50	1.66	1.5
	50-500	1.66	7.5
	500-2000	1.00	15.0
Transverse.....	5-50	1.66	0.6
	50-500	1.66	1.5
	500-2000	1.00	3.0
<i>b. Random</i>			
Thrust.....	20-2000	4.0	11.5
Transverse.....	20-2000	4.0	11.5
<i>c. Resonance</i>			
Thrust.....	100-120	0.5	52.5
	550-650	0.5	60.0
Transverse.....	45-65	0.5	15.0
	550-650	0.5	10.0

6. Capacity at Low Temperature

The cell shall be charged (as in A-3) and placed in a chamber maintained at 30° F. The cell shall be allowed to stand on open circuit for 1 hour and then discharged at a constant current of 0.12 ampere to an end voltage of 1.0 volt. The discharge capacity shall be 0.64 ampere-hour. This test shall be repeated for a total of two cycles.

7. High Rate Discharge Capacity

The cell shall be charged (as in A-3), allowed to stand on open circuit for 1 hour and then discharged at a constant current of 1.5 amperes to an end

voltage of 1.0 volt. The discharge capacity shall be 0.4 ampere-hour, minimum.

8. Charge Retention

The cell shall be charged (as in A-3), allowed to stand on open circuit for 30 days and then discharged at a constant current of 0.12 ampere to an end voltage of 1.0 volt. The discharge shall be 0.6 ampere-hour minimum.

9. Overcharging Rate

The cell, in an ambient of 112° F and at a vacuum of at least 10^{-4} mm Hg, shall be charged at a constant current of 0.065 ampere for a period of 96 hours. At the end of this period the ambient temperature shall be reduced to 100° F and the charge continued for an additional 30 days. The cell shall show no evidence of electrolyte leakage or change in physical dimensions. Following examination and/or test for electrolyte leakage, the cell at ambient temperature of 75° F shall be discharged at a constant current of 0.12 ampere to an end voltage of 1.0 volt. The cell capacity shall be 0.81 ampere-hour minimum at a temperature of 75° F.

10. High Current Discharge

The cell shall be charged (as in A-3). The cell shall be subjected to 10 pulse loads each at 10 amperes for 10 milliseconds duration. During discharge the voltage shall be 1.0 volt minimum.

11. Operational Life

To expedite the tests, the operational life tests may be conducted in parallel with those just described. A minimum of 20 cells, after being subjected to and meeting the requirements for acceptance, shall be subjected to the life cycling tests listed below. During the cycling tests, the ambient pressure shall be a vacuum of at least 10^{-4} mm Hg. The rate of change of the ambient temperature shall be 5° F/minute.

Cycle number	Charge-dis-charge condition	Ampere	Duration, hr.	Ambient temp., °F
1 through 5	Charge	0.065	16	75
	Discharge	0.120	(¹)	75
6	Charge	0.065	167	100
	Discharge	0.120	1	30
7 through 50	Charge	0.065	5	75
	Discharge	0.120	1	75

¹ To an end voltage of 1.0 volt.

Repeat cycles 1 through 50 for a total of 200 charge-discharge cycles. On the last (200th) cycle, the cell discharge capacity to an end voltage of 1.0 volt shall be measured. This capacity shall be 0.5 ampere-hour minimum.

12. Capacity at High Temperature

The cell shall be charged (as in A-3) and placed in a chamber maintained at 100° F. The cell shall be allowed to stand on open circuit for 1 hour and then discharged at a constant current of 0.12 ampere to an end voltage of 1.0 volt. The discharge capacity shall be 0.73 ampere-hour minimum.

GLOSSARY

AH.....	Ampere-hour (used in specifying capacity of a cell).
anode.....	In general electrochemical terminology, the electrode of a cell at which electrochemical oxidation occurs. In a battery, the negative electrode during discharge.
battery.....	A group of cells, either primary or secondary, connected in series.
C.....	Capacity of cell in ampere-hours.
cathode.....	In general electrochemical terminology, the electrode of a cell at which electrochemical reduction occurs. In a battery, the positive electrode during discharge.
cell capacity.....	The quantity of electricity which a cell can store, expressed in ampere-hours or other current-time units.
current efficiency..	The proportion of an electric current which produces the desired chemical effect, as "charging efficiency." (See text for typical values.)
cycle.....	In battery terminology, a single sequence of charge and discharge.
depth of discharge.	The proportion of the nominal capacity removed from a cell during each discharge portion of a cycle, expressed in per cent.
diffusion.....	Random movement of a dissolved particle by virtue of thermal motion, not affected by an electric field.
electrolyte.....	In batteries, usually an aqueous solution of an ionized inorganic compound; serves to conduct electricity within the cell by ionic migration.
ion.....	A conducting particle of the electrolyte; in alkaline batteries, potassium ion (K^+) and hydroxyl ion (OH^-); conduction is by migration.
migration.....	Directed movement of an ion of the electrolyte in an electric field; to be distinguished from diffusion.
plate.....	An electrical conductor which gives mechanical support to the active materials of a cell; serves to bring electrons to and from the active materials.

- power efficiency . . . The proportion of energy recovered from a storage system, i.e., output power/input power, expressed in per cent. (See text for typical values.)
- primary cell A cell which is intended for "one-shot" service (not rechargeable).
- rechargeable
primary cell. A cell which is ordinarily used in "one-shot" service, but which is capable of a limited number of charge-discharge cycles (frequently 5-10); term almost exclusively applied to silver-zinc missile batteries.
- secondary cell A cell which can be recharged hundreds to many thousands of times.
- specific energy The energy storage ability of a battery on a weight basis, usually expressed in watt-hours per pound; sometimes given on a volume basis in watt-hours per cubic foot.

APPENDIX

MANUFACTURERS OF SEALED SPACE BATTERIES

1. Sonotone Corporation, Elmsford, New York
Nickel-Cadmium
Wide range of capacities
2. Gulton Industries, Incorporated, Metuchen, New Jersey
Nickel-Cadmium
3 AH, 6 AH, 12 AH, and 20 AH
Silver-Cadmium
7 AH
3. General Electric Company, Hudson Falls, New York
Nickel-Cadmium
4. Yardney Electric Corporation, 40-52 Leonard Street, New York 13, New York
Silver-Cadmium
Wide range of capacities
0.14 AH to 150 AH
Silver-Zinc
5. The Electric Storage Battery Company, Missile Battery Division, 2510
Louisburg Road, Raleigh, North Carolina
Silver-Zinc
4 AH, 7.5 AH, and 25 AH
6. Delco-Remy Division, General Motors Corporation, Anderson, Indiana
Silver-Zinc
7. Gould-National Batteries, Incorporated, 2630 University Avenue, S.E.,
Minneapolis-Minnesota
Nickel-Cadmium
Wide range of capacities
Silver-Cadmium
Silver-Zinc
8. Telecomputing Corporation, Power Sources Division, 3850 Olive
Street, Denver, Colorado
Silver-Cadmium

9. The Eagle-Picher Company, Couples Department, P.O. Box 290, Joplin, Missouri
Nickel-Cadmium
Silver-Cadmium
Silver-Zinc

TEST FACILITIES

In addition to the facilities operated by battery manufacturers and by contractors responsible for the design and construction of space vehicles, the following organizations are equipped to conduct life tests on sealed space batteries:

1. Inland Testing Laboratories, Cook Electric Company, Dayton, Ohio
2. Naval Ammunition Depot, Crane, Indiana
3. Associated Testing Laboratories, Wayne, New Jersey
4. Dayton T. Brown, Bohemia, Long Island, New York
5. General Testing Laboratories, Newark, New Jersey

POWER INFORMATION CENTER OF THE INTERAGENCY ADVANCED POWER GROUP

This center serves as a clearing house for information on power systems of all types. The address is: Power Information Center, Moore School Building, 200 South 33d Street, Philadelphia 4, Pennsylvania, Telephone 215-382-8683

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